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PROCEDURES MANUAL TERRESTRIAL EFFECTS ACIDIC PRECIPITATION IN ONTARIO STUDY (APIOS)

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Ministry of the Environment

Ontario

The Honourable
Andrew S. Brandt
Minister

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Deputy Minister

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PROCEDURES MANUAL

TERRESTRIAL EFFECTS

ACIDIC PRECIPITATION IN ONTARIO STUDY (APIOS)

APIOS Report No. 007/83

Editor: H. D. Griffin
Northwestern Region

TECHNICAL SUBCOMMITTEE
TERRESTRIAL EFFECTS WORKING GROUP
ONTARIO MINISTRY OF THE ENVIRONMENT

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PREFACE

This manual briefly outlines the procedures followed in the terrestrial effects program of the Acidic Precipitation in Ontario Study (APIOS). The manual was prepared to ensure a standardized approach to terrestrial studies carried out by the Ontario Ministry of the Environment throughout the province. It also serves as a source of information to other agencies which may be interested to learn of our study methods.

The manual comprises four parts: vegetation studies, soil studies, biogeochemical studies, and laboratory analysis. The methods described are those in use at the time the manual was prepared. The Technical Subcommittee of the Terrestrial Effects Working Group plans to periodically review the manual and to revise it as required. Many of the methods outlined are those in regular use by the Ministry or are generally recognized as acceptable by the scientific community. Procedures representing novel approaches (eg. parts of the biogeochemical program) have been reviewed and approved by scientists within and outside the Ministry.

Principal contributors to the manual were: W. Gizyn and A. Kuja, Air Resources Branch (vegetation studies); D. Dimma and M. Griffith, Air Resources Branch (soil studies); W. McIlveen, Northeastern Region (biogeochemical studies); and A. Neary, Laboratory Services and Applied Research Branch (laboratory analysis).

A. VEGETATION STUDIES

BASELINE SAMPLING

Objective

There are many potential effects of acidic precipitation on terrestrial ecosystems, some of which may lead to changes in foliage chemistry. These effects may occur through direct mechanisms, such as deposition of sulphur and nitrogen, or through accelerated leaching of foliage. Indirect mechanisms, such as changes in nitrogen transformations in soil, leaching of soil bases, increased availability of metal elements, or reduced availability of phosphorus to plants, may also play a role.

The purpose of baseline sampling is to establish the current status for chemical constituents in Ontario forest vegetation. This data base will enable future changes caused by acidic precipitation or other long-range transport pollutants to be detected.

Site Selection and Description

To relate changes in foliage chemistry to pollutant deposition, the location of survey sites are as close as possible to APIOS deposition monitoring sites.

Each sampling site is in a secure location, preferably on publicly-owned land. The area is forested, and free of major recent disturbances such as fire, clear cutting, or cultivation. Some assurance that disturbance will not likely occur in the future is also required. Forested lands within provincial parks or conservation areas often meet such criteria.

The site contains as many as possible of the following tree species: sugar maple (Acer saccharum), white birch (Betula papyrifera), trembling aspen (Populus tremuloides), white spruce (Picea glauca) and eastern white pine (Pinus strobus). These species have been selected as common denominator baseline forest

trees across the province. However, because of the wide range in climatic and soil conditions across the province, these species will not all be available at all sites.

Baseline sampling sites are located away from local sources of atmospheric contaminants. Sample trees are at least 100 m from gravel roads, at least 50 m from paved roads, and at least 50 m from the edge of the forest canopy.

Sites are identified by UTM coordinates and a sketch map is prepared to show sampling location in relation to permanent local landmarks. Sufficient detail is included to permit future site relocation. Photographs are taken of the site and its access.

Sampling Procedure

Triplicate representatives of each of the four common denominator species are selected as sample trees. These trees must be healthy, and free of signs of bole damage or crown dieback. A diagram is prepared to indicate the relative distances and compass bearings between the individual sample trees. Plastic tags are prepared showing the program, site number, tree species and replicate number. For example, a tag reading "APIOS - S7 - PG 3" would represent the APIOS program, site #7, Picea glauca, replicate 3. These tags are attached to the stem of the tree with a stainless steel nail, which is only partially driven in to permit stem diameter growth. Alternatively, numbered tags may be used.

Branches are cut from the middle, or lower-middle portion of the crown. To increase the possibility of obtaining a representative sample, the lowest branch is avoided, even though it is the most accessible. Pruning poles of sufficient strength and length are recommended as sampling devices to reach such branches, which are often more than 15 m above the ground. To avoid contamination, the falling branch is not permitted to contact the soil. Foliage-bearing twigs are cut from the branch and placed in plastic bags. Plastic gloves are worn to prevent sample contamination. Appropriate sample numbers are attached to the sample bags.

Sample Preparation and Submission for Analysis

Samples are refrigerated as soon as they are brought to the processing laboratory. The leaves, including petiole, are first removed from the twigs. Damaged or infected leaves are discarded. For white pine, the current year's foliage is separated from older foliage and the two samples are processed separately. For white spruce, the current year's foliage is separated from 1-year-old foliage and the two samples are processed separately: foliage more than 1 year old is discarded. Segregation of individual years of growth, other than current growth, is not recommended, since identification of different ages of foliage is often difficult.

Sorted samples are placed in kraft paper bags and dried for 30 hours at 80°C in a forced draft oven. Dried tissue is ground to pass through a 1 mm screen in a stainless steel Wiley mill and is collected in a glass jar with a plastic or pulp-lined lid.

Baseline samples are submitted to the Ministry's Toronto laboratory for the following analyses: total sulphur, nitrogen, phosphorus, potassium, chloride, calcium, magnesium, sodium, aluminum, manganese, iron, cadmium, copper, molybdenum, nickel, lead and zinc. The test group for these parameters is TEAPS 5 and the individual LIS (Laboratory Information System) test names, in the same order as above, are: SSUT, NNTKUR, PPUT, KKUT, CLUT, CAUT, MGUT, NAUT, ALUT, MNUT, FEUT, CDUT, CUUT, MOUT, NIUT, PBUT and ZNUT.

Variability Study

A sampling variability study has recently been conducted to determine the effects of tree size, crown position of sample, and preferred sampling date in the growing season. Changes in the foregoing sampling procedures may be recommended when the data from this study have been reviewed.

SIMULATED ACID RAIN STUDIES

Objective

The objective of these studies is to document the effects of acidic precipitation on vegetation under controlled conditions. Experiments can be carried out to determine: threshold doses causing injury symptoms, biochemical and physiological effects; relative sensitivity of agricultural crops and forest tree species; growth and yield response of plants to different rain acidities; effects on seedling establishment; effects caused by interactions with gaseous pollutants and with plant pathogens.

The findings of these studies will assist in developing abatement programs to control acid rain.

Program Management

Simulated acid rain studies in the APIOS progam are carried out at the controlled environment laboratory at Brampton, Ontario, by the Ministry's Phytotoxicology Section, Air Resources Branch. All proposed experiments are first reviewed by the Technical Subcommittee, Terrestrial Effects Working Group, which sets priorities and ensures that the studies comply with established objectives.

Equipment

Simulation Chambers

Four chambers, permitting the simultaneous application of four different simulated rain solutions are available for experimental work. The chambers are housed in a single framework 7.3 m high, 4.9 m wide, and 1.2 m deep, constructed of aluminum angle ("Dexion 225"). Each chamber floor is 1.2 by 1.2 m. A steel platform along the top of the structure provides access to nozzles and light fixtures. Figure 1 (page 12) is a schematic diagram of a chamber and ancillary control apparatus.

The chamber walls consist of an outer layer of extruded styrofoam and a water-resistant inner layer of white, laminated, plastic. Chamber walls are secured to the aluminum frame with stainless steel bolts. Seams and joints of inner walls are sealed with silicone to prevent leakage. A clear, plexiglass door, 1.14 m high and 0.8 m wide, provides access to each chamber at a point just above the turntable. Chamber floors are constructed of fibreglass-coated, 20-mm plywood, and drained with ABS plastic piping, 5 cm in diameter.

A turntable, which permits uniform distribution of simulated rain, is located on the floor of each chamber. Each turntable is 1.1 m in diameter and is constructed of 20-mm plywood. It is driven by a central steel shaft connected to a 1/16 hp electric motor beneath the chamber floor. Each turntable rotates at 4 r.p.m. The weight of potted plants is supported by four pivoting caster wheels on the underside of the turntable. The turntable in each chamber can accommodate up to 80, 10-cm pots; 36, 16-cm pots; or 20, 22-cm pots. However, about half this number is more manageable so that test plants do not touch each other. Each turntable is fitted with a skirted PVC cover, which is removable for cleaning or maintenance.

To achieve terminal velocity, droplets of the simulated rain solution are dispersed from a nozzle 5.33 m above the centre of each turntable. The nozzles are fabricated from a stainless steel body, and a PVC nipple (Model SRN 303, Bete Fog Nozzles Inc., Greenfield, Mass.). These nozzles produce droplets 1 mm in diameter, a size within the range found in natural rain. The droplets are dispersed from 28 orifices under low pressure (2 - 3 psi). Each nozzle is attached to the centre of a plexiglass levelling plate, which can be adjusted to produce the best "rain" distribution on the turntable below. Nozzles are connected with 6-mm O.D. polyethylene tubing and compression fittings to the rain application system at the base of the chambers.

To simulate light conditions during natural rainfall, a "Luminaire" fixture containing a 1000-watt, metal halide lamp

(GE, MVR 1000) is mounted above each chamber nozzle. To obtain optimum light at the turntable, reflective, heavy-gauge, aluminum foil is placed around each fixture.

The tops of the four chambers are presently uncovered. They will be sealed when plans for temperature and humidity control are implemented.

Rain Application System

Simulated rain solutions are stored in 26-litre "Nalgene" carboys stored near control panels which govern the application of the solutions in the four chambers. During treatment applications, the pressure in each carboy is maintained at 15 psi with a regulator mounted in the line from the compressor supplying filtered, dry air. Three electric timers may be programmed to supply rain simulants at a continuous rate up to 6 h, or intermittently for intervals up to 12 min each within any given period of up to 6 h. The timers activate solenoid valves which control the flow of solutions from the carboys to the dispersal nozzles. Flow rates are controlled by rotometers. Between 0.5 and 2.5 cm of simulated rain per hour is applied to test plants with this system when operated in the continuous mode. A rate of 1.0 cm per hour gives maximum coverage of the turntable.

Simulated Rain Solutions

A treatment range of pH 2.6 to 5.6 has been selected for simulation experiments, based on the pH of "normal" rain and the current pH range of rainfall in Ontario. A similar range is used in laboratories in the United States. Eight pH levels are presently used in the Brampton chambers to determine threshold effects and to construct dose-response curves: 2.6, 3.0, 3.4, 3.8, 4.2, 4.6, 5.0 and 5.6.

The composition of stock solutions prepared for simulation experiments is based on the chemistry of rainfall monitored in Ontario. Dilution of stock solution produces a control simulant solution (pH 5.6) with the following ionic composition:

Na^+ (0.1 mg/ℓ), K^+ (0.06 mg/ℓ), Mg^{++} (0.1 mg/ℓ), Ca^{++} (0.4 mg/ℓ), Fe^{++} (0.01 mg/ℓ), NH_4^+ (0.35 mg/ℓ as N), Cl^- (0.74 mg/ℓ), NO_3^- (0.35 mg/ℓ as N), and $SO_4^=$ (0.66 mg/ℓ).

The pH of each acidic rain simulant is obtained by adding a measured amount of acid stock solution to the control solution. The acid stock solution is a 1.0 Normal or 0.1 Normal mixture of reagent grade sulphuric acid and nitric acid, with a 2.5:1 weight ratio of sulphate to nitrate. The 1.0 Normal stock solution is used to prepare solutions of pH 2.6 or 3.0, while the 0.1 Normal solution is used for simulant solutions in the range of pH 3.4 to 5.0. The sulphate to nitrate ratio is based on current Ontario rainfall. If future monitoring detects a change in the ratio in ambient rainfall, the ratio in simulant solutions will be adjusted appropriately. All stock solutions are stored in opaque, 1-litre "Nalgene" containers at 4°C, and are equilibrated at room temperature before use.

Rain simulants are prepared in 25-litre batches directly in the "Nalgene" carboys. Water for dilution of stock solutions is provided by a "Culligan Aqua Summa" water purifier which uses reverse osmosis and a mixed deionizing resin-bed cartridge. This unit produces 32 litres of ultra-pure water per hour, at a resistivity of 18 megohm. Each batch of simulant must be within 0.1 pH unit of the desired pH. Samples of simulants and deionized water are routinely submitted to the Ministry's Toronto laboratory for analysis of conductivity, pH, Gran acidity, SO_4, NO_3, NH_3, Ca, Na, K, Cl, PO_4, Fe, Pb, Zn, Cu, Ni and Cd.

Preparation of Test Plants

Soil mixtures are prepared from Ontario Ministry of Agriculture and Food recommendations for food crops. Pot size for each experiment is based on plant size and the duration of the experiment. To avoid toxic effects on hypocotyl development, only the bottom half of each pot has fertilized soil, with the upper half containing unfertilized soil.

In experiments to study direct effects of acid rain on plant foliage, rain simulants are excluded from the soil by mounding it about 2 cm above the pot rim and covering it with thin, plastic sheeting secured by rubber bands. The sheeting is sufficiently loose to allow the soil to "breathe". Two short, cross-shaped slits are cut in the centre of the plastic film through which seeds are sown. Pots covered in this manner must be irrigated from below.

All agricultural seeds are obtained from registered suppliers and stored at 4°C. Forest tree species may be collected as seedlings from natural areas or aquired as transplants from Ontario Ministry of Natural Resources nursery stock. Seed age and viability is recorded. Seeds are usually sown four to a pot and, after germination, thinned to one healthy individual. Pots are normally irrigated by placing them in plastic trays containing 1-2 cm deionized water, except when an experiment calls for all moisture to be supplied from rain treatments.

Thirty replications per treatment are usually desirable for statistical analysis, but may not be possible because of space limitations. After treatment, all pots are placed in random positions on greenhouse benches to reduce effects caused by differences in light intensity in different locations of the greenhouses. Temperature and humidity in the greenhouses are contolled and recorded. Incoming air is filtered to remove gaseous and particulate pollutants. Each of the two greenhouses is also equipped with a mechanically-controlled, heavy-gauge, polyethylene curtain to partially control incoming and outgoing radiation through the greenhouse roof. Fluorescent and incandescent lighting, controlled by timers to provide extended day length, is also available. During experiments, light is measured three times daily at three points along each bench where test plants are placed, using a "LICOR" integrating radiometer/ photometer (Model L1-188) with quantum sensor.

Treatment Applications

All pots are carefully handled in the early seedling stage to avoid damage to fine roots. Pots are arranged in a circle on the turntable and are equidistant from its centre. When the rain treatment has ended, plants are carefully removed from the turntable so that droplets on the foliage are not disturbed. To account for differences between chamber environments or nozzles, rain simulants are rotated among the four chambers so that all chambers receive each treatment during any experiment. Each nozzle system is briefly flushed with deionized water between treatments.

If simulants are the only source of water, treatments usually must be applied every second day to avoid moisture stress. A standard rain gauge on each turntable measures the amount of simulant applied. During treatments, beakers are placed on the turntables to collect samples of simulant for pH and conductivity analysis. Each beaker is placed inside a 30-cm length of PVC pipe on which is centred a large, polyethylene funnel to collect droplets. Replicate samples of each treatment are submitted for analysis of parameters listed under "simulated rain solutions".

Untreated control plants are grown in the greenhouses, but receive no simulants. They are watered with deionized water applied directly to the soil in quantities equivalent to those received by test plants. They also receive the same amount of light as test plants and are placed in a chamber for the same duration as plants which receive treatments. Temperature and humidity are measured in each chamber just before and after a treatment, with a Cole Parmer LCD digital thermohygrometer.

Observations and Harvest Procedures

The occurrence of foliar injury is recorded by notes and photographs. Colours are described with Munsell colour charts. Germination, seedling establishment, shoot height, numbers and sizes of leaves, and flower development are also recorded.

In experiments to determine effects on growth or yield, plants are removed from pots with soil intact around the roots. Soil is gently washed from the roots in a plastic tub containing warm water. The washed roots are then dried carefully on paper towels and separated from the rest of the plant. Shoot and root fresh weights are immediately measured to the nearest hundreth gram. Weighed material is placed in labelled paper bags (one plant per bag) and dried for about 48 h at 80°C in a forced draft oven. Dried material is reweighed. For very small seedlings, weights may be recorded to the nearest thousandth gram. Individual specimens may be saved for histological study or herbarium records.

Additional Experimental Facilities

Fumigation Chambers

Four controlled environment chambers are available at Brampton to determine effects on plants of exposure to controlled levels of gaseous pollutants such as sulphur dioxide, ozone, and ethylene, either singly or in combination. Air supplied to these units is filtered to remove air pollutants. Temperature, humidity and day length are controlled. These facilities are used together with the simulated acid rain chambers, to determine the combined effects of acid rain and other pollutants.

Test Garden

An outdoor garden of just under 1 ha has been established at Brampton. Most of this area has a sandy loam soil 30 cm deep over clay. Power is supplied to the site through four outlets and there is a buried water line for irrigation.

Mobile Exclusion Canopies

Three mobile rain exclusion canopies are now under construction at Brampton and are expected to be ready for use in 1984. These canopies will enable the Ministry to carry out simulation

experiments with established crops under conditions which are more natural than those using potted plants grown in a greenhouse. The canopies will exclude natural rain from the test area, so that the effects of the simulated rainfall alone can be studied. Simulated rainfall will be applied to treatment plots through nozzle systems mounted in the canopies.

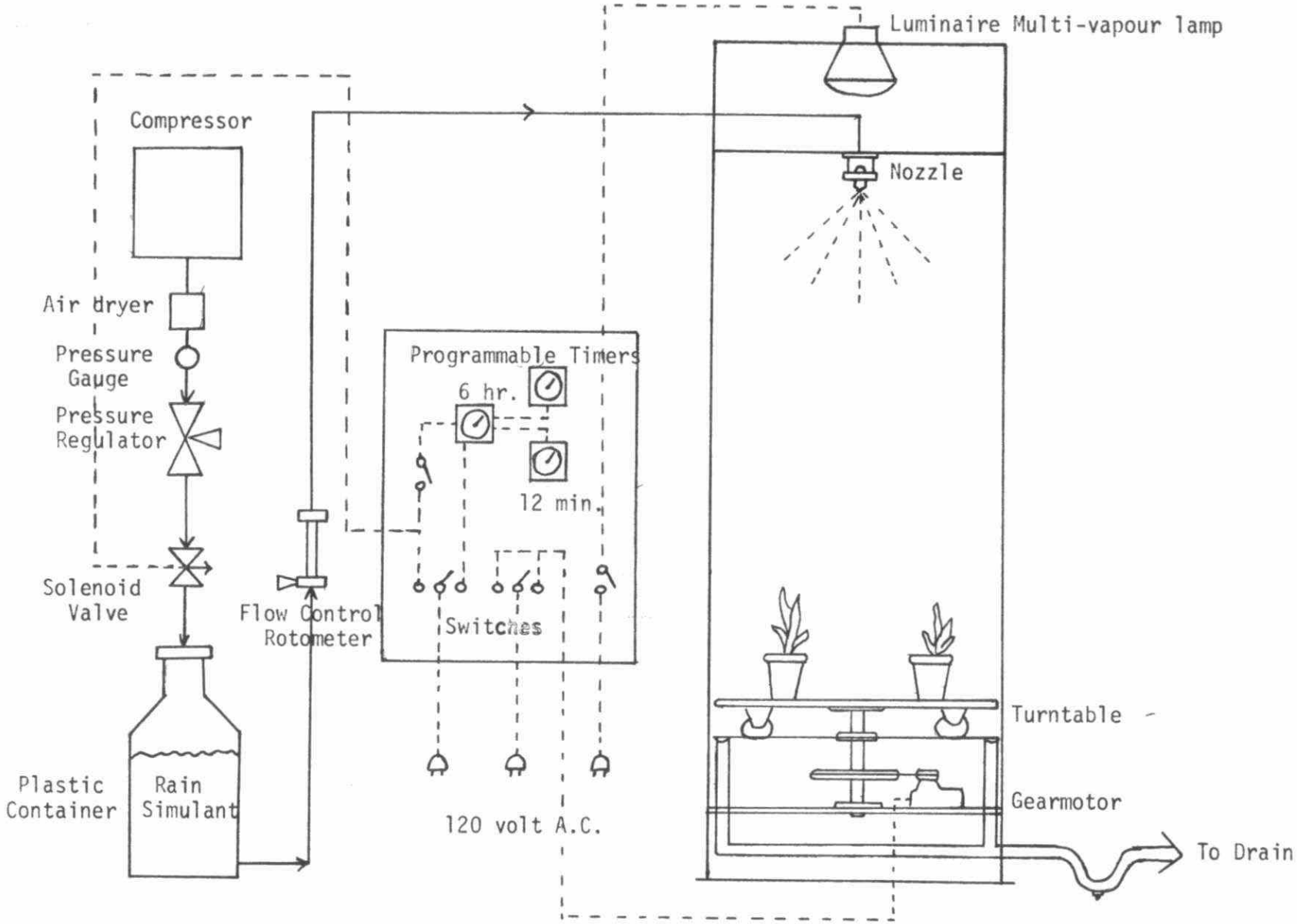


Figure I. Schematic diagram of indoor rain simulation chamber (for clarity, only one of four chambers is shown).

B. SOIL STUDIES

BASELINE SAMPLING

Objective

The principal objective of this study is to establish a reliable and uniform data base for soils across the province. The data base will (1) provide current data to identify future trends, (2) enable development of laboratory experiments to define criteria for the sensitivity of soils to acidification, and (3) provide information required for sensitivity mapping of Ontario soils.

Site Selection and Description

Baseline sites are located on undisturbed soils. Provincial parks, conservation areas and Crown land offering reasonable access and long-term security are generally best suited for baseline sampling.

To enable soil chemistry and precipitation chemistry to be correlated, at least one soil site on each important landform is sampled within about a 20 km radius of APIOS deposition monitoring locations across the province. A variety of landforms and soil types should also be sampled to enable the preparation of soil sensitivity maps. Variations in acidic input, climate, geology and vegetation should also be considered.

Site locations are identified by UTM coordinates and a sketch map is prepared showing the sampling location in reference to permanent local features. Sufficient detail is included to permit site relocation. The site is described according to the guidelines in the "Field Manual for Describing Soils" (Institute of Pedology, University of Guelph).

Sampling Procedure

A pit, approximately 1 m^2, is dug to a depth sufficient to permit sampling of the parent material. Soil profiles are

described according to criteria adopted by the "System of Soil Classification for Canada" (publication no. 1455, revised 1974, Canada Dept. of Agriculture). The soil pit is photographed and a sketch is drawn of one of the faces sampled to show major soil horizon boundaries and the positions of stones, root masses, and sampling points. Figure 2 (pages 21 and 22) is a blank form of the type used to record field data.

Beginning at the deepest horizon, duplicate samples, each weighing approximately 1 kg, are collected with a hand trowel from opposite sides of the soil pit and placed in labelled plastic bags. For special studies, undisturbed soil of known orientation may be sampled with Kubiena boxes, or equivalent containers, by carefully pressing the box or container into the wall of soil pit and removing the sample and container simultaneously. When sampling is concluded, soil horizons are returned to a pit in the reverse order from which they were removed, to achieve the least possible disturbance of the sampling site.

Present plans call for a sampling frequency of approximately once every 5 years for baseline sites in Ontario. To reduce potential effects of seasonal variations on soil properties, repeat samples should be collected at the same time of year as in the original survey, from new pits adjacent to the original ones.

Sample Preparation and Submission for Analysis

To minimize physical and chemical degradation of the soil, samples are spread out on non-metallic trays and air dried for 48 hours within a few days of collection. Dried samples are disaggregated with a porcelain mortar and pestle or motorized grinder, then sieved to two particle-size fractions: <10 mesh and <100 mesh, ASTM. From each sample, at least 150 g of the <10-mesh fraction are placed in a glass jar and submitted for analysis. Approximately 5 g of <100-mesh soil are submitted in glass vials for analysis of metals, carbonates, organic carbon, and pyrophosphate iron and aluminum. The remainder of the disaggregated sample is stored in cardboard or glass containers of suitable size.

The following analyses are performed on baseline samples: pH (distilled water and calcium chloride); exchangeable calcium, magnesium, potassium, and aluminum; cation exchange capacity; pyrophosphate and dithionite extractable iron, aluminum and manganese; organic carbon; total carbonates; total nitrogen; plant available phosphorus; soluble sulphur and aluminum; heavy metals (Cu, Ni, Pb, Zn); and texture (particle size). The LIS (Laboratory Information System) test groups for these analyses are TEAPS 1 plus TEAPS 6, and the LIS test names (in the same order as above) are: PHEW, PHECA, CAESC, MGESC, KKESC, ALESC, CEC, FEEPY, ALEPY, MNEPY, FEEDI, ALEDI, MNEDI, COD, CCO3UR, NNTKUR, PPO4SB, SSO4EW, ALECA, CUUT, NIUT, PBUT, ZNUT, SAND, SILT, CLAY. Figure 3 (pages 23 and 24) is a blank form of the type used to record the data.

SOIL VARIABILITY

Objective

The objective of this study is to document the natural spatial and seasonal variability in some baseline soil parameters at selected study sites.

Site Selection

Within the study area, a sampling plot measuring 10 m by 10 m is located at a site representative of the general study area.

Sampling Procedure

A grid (Figure 4, page 25) is superimposed over the sampling plot and 33 sampling points are marked with 25 cm wooden stakes. Using a stainless steel corer, 45 cm long and 30 mm in diameter, at least five soil cores are obtained radially around each stake. Core depth should extend to the C horizon, or to bedrock if no C horizon is present. If the C horizon is below the sampling range of a 45 cm corer, the arm of the corer can be extended to reach

the required depth. Each core is separated into its component horizons and the horizons from each of the cores are pooled to form one sample. The sample is then placed in a numbered plastic bag. Because of limitations in resources, the Ministry is currently sampling only the A and B horizons in its variability study. The C horizon, and A and B subhorizons may also be sampled separately, if present in sufficient quantity.

Study sites are sampled in the spring, summer and fall. It is anticipated that two years of data will be adequate for this investigation.

Sample Preparation and Submission for Analysis

Samples are prepared for analysis in the same manner specified for baseline sampling. The same analyses are also performed, unless the size of sample is insufficient. Top priority is given to the determination of soil pH (water and calcium chloride), exchangeable cations, organic carbon, soluble aluminum and sulphur and texture.

SOIL COLUMN LEACHING EXPERIMENTS

Objective

The objective of these studies is to predict the long-term effects of acidic precipitation on soil under controlled conditions. Laboratory experiments will document changes in soil chemistry and processes resulting from different acid loadings. Study results will be used to develop sensitivity criteria for the preparation of soil sensitivity maps for the province. The data will also be used to predict the number of years for different acidities of precipitation to affect different types of Ontario soils. Information for the biogeochemical study model will also be generated.

Preparation of Soils

Experiments in Toronto use intact columns of A, B and C horizons from a range of soil types commonly found in southern and central Ontario. The soils are placed in buchner funnels (17 cm diameter, 9 cm high) in the field, in vertical combinations of A, AB, and ABC horizons. The separation of horizons before treatment permits the identification of horizons altered by acidic solutions.

Similar studies in Thunder Bay use intact profiles (A, B and C horizons combined) from a Brunisolic soil in a watershed study area in northwestern Ontario. Each column is 100 cm long and is contained in PVC tubing, 15 cm in diameter and 120 cm long.

Both the Toronto and Thunder Bay experiments apply simulated acidic solutions at the rate of 500 ml per week. The Toronto application rate represents 1 year of average rainfall per year of experiment. In Thunder Bay, the application rate is equivalent to 2 years of rain during 1 year of experiment. The soil leachate from both studies is analysed monthly for major cations, anions, and metals. The sample preparation methods and list of parameters analysed are the same as those for soil leachate in the biogeochemical study (see pages 40 and 41).

Equipment

The application apparatus for each soil column in the Toronto study consists of an acrylic lower reservoir to which simulated precipitation is drip-fed from an upper reservoir (Figure 5, page 26). The precipitation escapes from the lower reservoir via 19 evenly spaced polyethylene capillary tubes (Figure 6, page 27). When simulated precipitation enters the lower reservoir, hydraulic pressure is increased uniformly and drops flow from the capillary tubes. The lower reservoir takes a single stream of large drops emanating from the upper reservoir and transforms it into 19 slower streams of smaller drops which fall on the soil column.

The application apparatus in the Thunder Bay study is similar to that in the Toronto study, but differs in some details. There is an inverted polyethylene funnel over the top of each column. Simulated rain entering the base of the funnel falls on a layer of polyethylene screening (1.5 mm mesh) which lies on a polyethylene disc. The disc is 2 mm thick, 15 cm in diameter, and contains 120 evenly-spaced holes, each 2 mm in diameter. The disc is held in position 10 cm above and the solution which passes through the disc is evenly dispersed over the surface of the soil column.

The time required to feed simulated precipitation into the application apparatus is shortened by attaching each upper reservoir via a series of Y or T connectors to one of three large master reservoirs. These master reservoirs contain different simulated rain solutions. Each upper reservoir is outfitted with a three-way valve at the point of solution entry. The application apparatus is manipulated to produce rainfall rates in the range of 1.27-2.54 cm/h by adjusting the outflow from the upper reservoir using a two-way valve. Rain drops produced by the apparatus are in the range of 2.0 to 3.0 mm in diameter.

Simulated Rain Solutions

A treatment range of pH 2.0 to pH 5.6 has been used in simulation experiments, based on the pH of "normal" rain and the current pH range of rainfall in Ontario. A stock solution is prepared by the Ministry's Toronto laboratory which simulates the average ionic concentration found in bulk precipitation in Ontario. The pH 5.6 solution has the following ionic composition: Na^{+} (0.1 mg/ℓ), K^{+} (0.06 mg/ℓ), Mg^{++} (0.09 mg/ℓ), Ca^{++} (0.37 mg/ℓ), Fe^{++} (0.01 mg/ℓ), NH_4^{+} (0.33 mg/ℓ as N), Cl^{-} (0.70 mg/ℓ), NO_3^{-} (0.32 mg/ℓ as N), $SO_4^{=}$ (0.64 mg/ℓ), and conductivity (9.2 μmhos/cm).

The pH of the solution is then adjusted using sulphuric acid. Samples of simulants and deionized water are routinely submitted to the Ministry's Toronto laboratory for analysis of the same parameters as the leachate.

BUFFERING CURVE STUDY

Objective

The determination of a soil's sensitivity to acidification is critical to the study of the effects of acidic precipitation on terrestrial and aquatic ecosystems. Buffering curve experiments are being undertaken to document changes in soil chemistry resulting from different acid loadings. The relationship of the slopes of soil buffering curves to the physical and chemical properties of soils throughout Ontario will provide a means for establishing sensitivity criteria required for the sensitivity mapping of Ontario soils.

Experimental Procedure

A 10 g aliquot of air-dried soil, sieved to less than 10 mesh, is saturated with 40 ml of reagent, stirred, and equilibrated for at least 1 hour. pH measurements of the soil suspension are made in reagents of increasing acidity (pH 5.6, 4.0, 3.5, 3.0, 2.8, and 2.5) to determine the rate of change of soil pH with inputs of acidity. Nitric, sulphuric, nitric-sulphuric and simulated acidic precipitation reagents are used to assess the response of a soil to different types of acids. A buffering curve is generated by plotting soil pH in each reagent against the concentration of H^+ added to the reagent (Figure 7, page 28). To better document changes in soil chemistry during soil acidification, supernatant solutions may be centrifuged, filtered, acidified and analysed for selected base cations and metals.

OPEN-TOP SOIL COLUMN STUDY

Objective

The objective of this inter-regional study is to determine the long-term chemical changes in soil exposed to different climate conditions and different levels of long-range atmospheric pollutants. This information will also supplement the findings of the soil baseline program.

Column Preparation

A total of 72 sections of PVC pipe, each 50 cm long and 15 cm in diameter, were filled with soil. Twenty-four of these columns contained a sandy soil from northwestern Ontario, 24 contained a northeastern Ontario clay soil, and the remaining 24 contained a silty soil from southern Ontario. Each column comprised a well-mixed A and B horizon. A plastic screen was positioned between the A and B horizons and was secured on the bottom of each pipe. Samples of the mixed A and B horizons from each region were sent to the Ministry's Toronto laboratory and analysed for the same parameters listed for baseline soils (see pages 14 and 15).

Distribution of Columns

The 72 re-constructed soil columns are distributed among three regions of the province (Northeastern, Northwestern and Southern) so that each region has 8 soil columns of a sandy soil from northwestern Ontario, 8 columns of a silty soil from southern Ontario and 8 columns of a clay soil from northeastern Ontario.

The soil columns are placed at field sites selected following the criteria used for A.P.I.O.S. event precipitation collectors. At each site, a trench was excavated to a depth of 60-70 cm. The soil columns were then placed in the trench, B horizon down, with the outer rims of the columns 10 cm apart.

The top of the PVC pipes are 4 cm above the surface of the ground. The trench was carefully filled in and soil was packed down around the pipes. Kentucky Bluegrass was sown on all soil columns and the area kept clear of weeds.

Sample Collection and Analysis

At intervals of 5, 10, 15 and 20 years after the start of the study, duplicate columns of each of the three soil types will be removed from the ground in each region. Soil will be removed from the columns and samples from the A and B horizons will be prepared for chemical analysis following the procedures outlined in baseline soil sampling (see pages 14 and 15).

Figure 2

APIOS - SOILS BASELINE STUDY

DEPTH (cm) HORIZON DESIGNATION

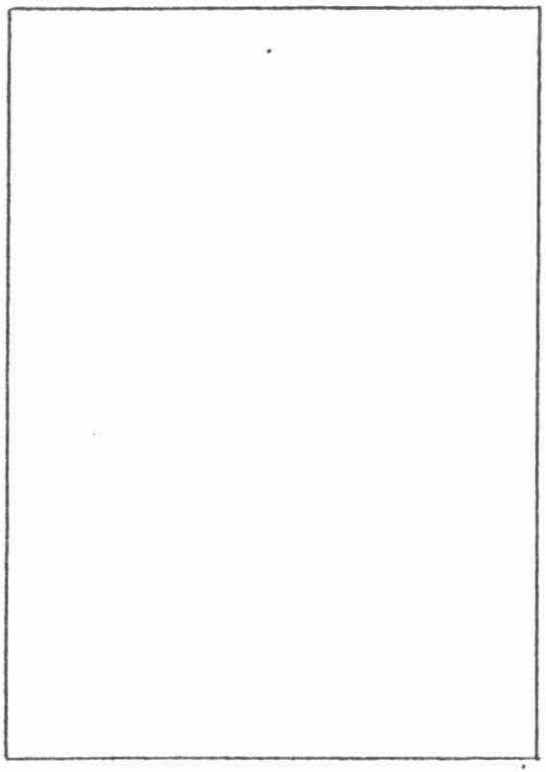
SITE: _____ LOCATION:

SAMPLE #: _____

PHOTOGRAPH #: _____ VEGETATION:

SAMPLED BY: _____

SITE #: _____



DEPTH TO FAINT MOTTLING: _____ cm

DEPTH TO PROMINENT MOTTLING: _____ cm

DEPTH TO G LAYER: _____ cm

DEPTH TO BEDROCK: _____ cm

PARENT MATERIAL: _____

SURFACE EXPRESSION: _____

SLOPE: _____

HORIZON	COLOUR	TEXTURE	STRUCTURE	HORIZON BOUNDARY	STONINESS	ROOTS

Figure 2

APIOS-SOILS BASELINE STUDY (CON'T)

DESCRIPTION OF SITE

**SEE: FIELD MANUAL FOR DESCRIBING SOILS (ONTARIO INSTITUTE OF PEDOLOGY)

location: _____ sample: _____

sampled by: _____ site #: _____

date: _____

1. slope: simple _____ complex _____

   slope class 1 2 3 4 5 6 7 8 9 10

   slope percent _____

   site position on slope A B C D E F G

2. soil drainage _____

3. mottle description _____

   mottle abundance _____

4. pore pattern moisture soil regime: perviousness: rapidly moderately slowly

   soil moisture regime: dry _____ fresh _____ moist _____ wet _____

5. forest humus classification _____

6. degree of decomposition for organic soils _____

7. types and classes of soil structure: type _____

   kind _____

   class _____

8. area percentage covered _____

9. stoniness _____

10. rock outcrop _____

Figure 3

SOIL PROFILE INFORMATION

Horizon *Depth*

Site: *Date:*

Location Code: *Parent Material:*

UTM: *Vegetation:*

Classification:

Landform: *Comments:*

Slope:

Sample No.	*Horizon*	*Depth (cm)*	*Colour*	*Sand (%)*	*Silt (%)*	*Clay (%)*	*pH (H_2O)*	*pH ($CaCl_2$)*	*Organic C (%)*	*Total Nitrogen (mg/g)*	*Ext. S (mg/g)*	*Ext. SO_4 (ug/g)*	*Avail. P (ug/g)*	*Avail. Al (ug/g)*

Figure 3

SOIL PROFILE INFORMATION (cont'd)

Site:

Classification:

Sample No.	Horizon	Exchangeable Cations (ug/g) Ca	Mg	K	Al	C.E.C. (m.e./100g)	Pyrophosphate (%) Fe	Al	Mn	Dithionite (%) Fe	Al	Mn	$CaCO_3$ (%)	Metals (ug/g) Zn	Cu	Ni	Pb

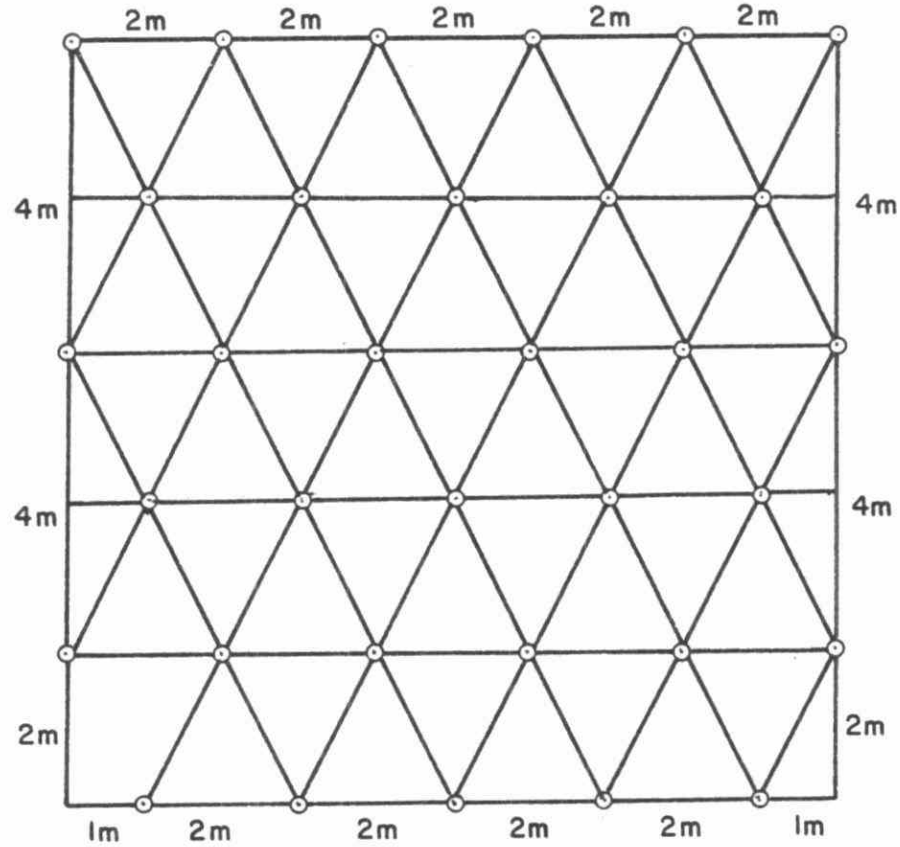


Figure 4. Sampling grid for soil variability study.

⊙ Sample site

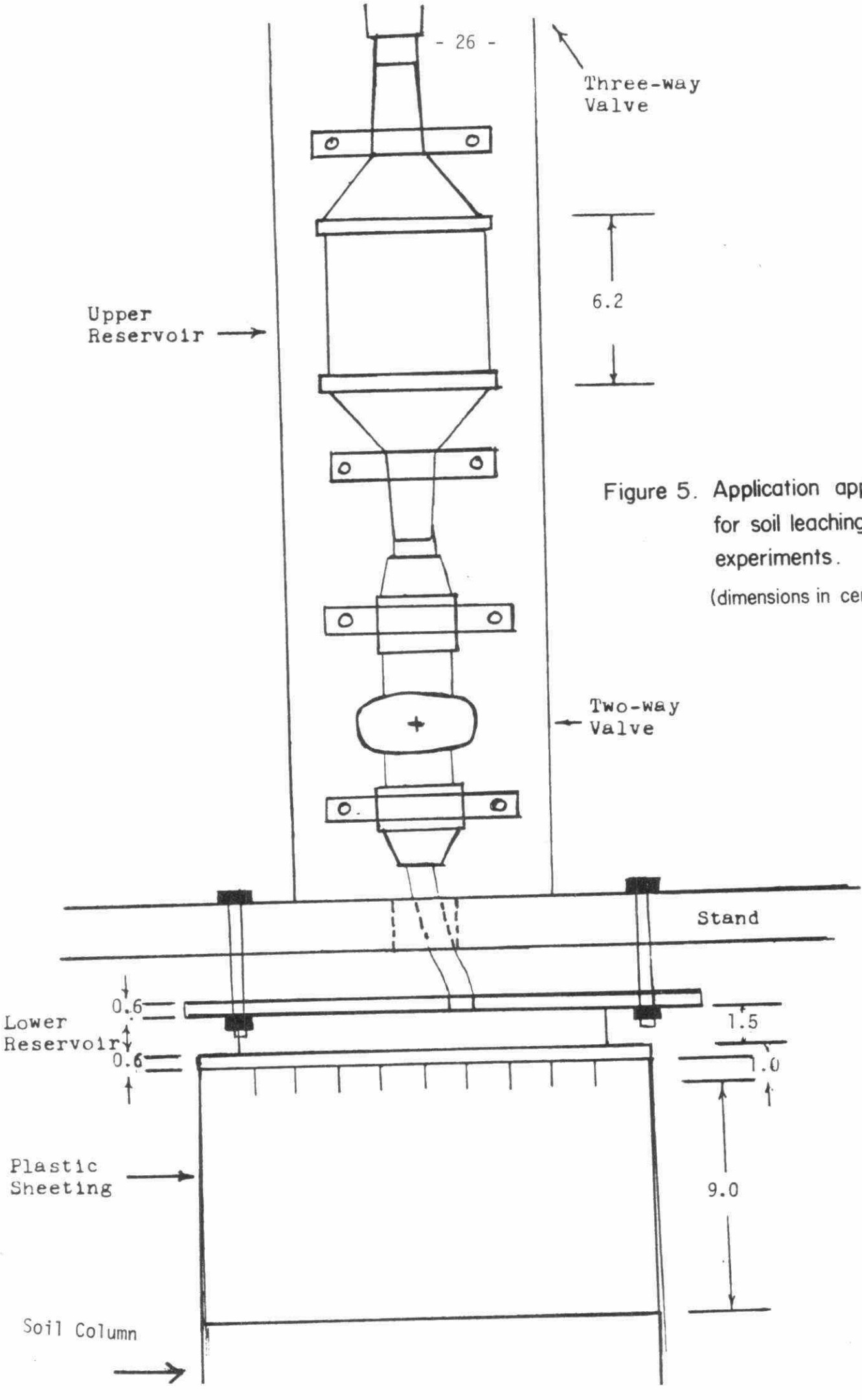
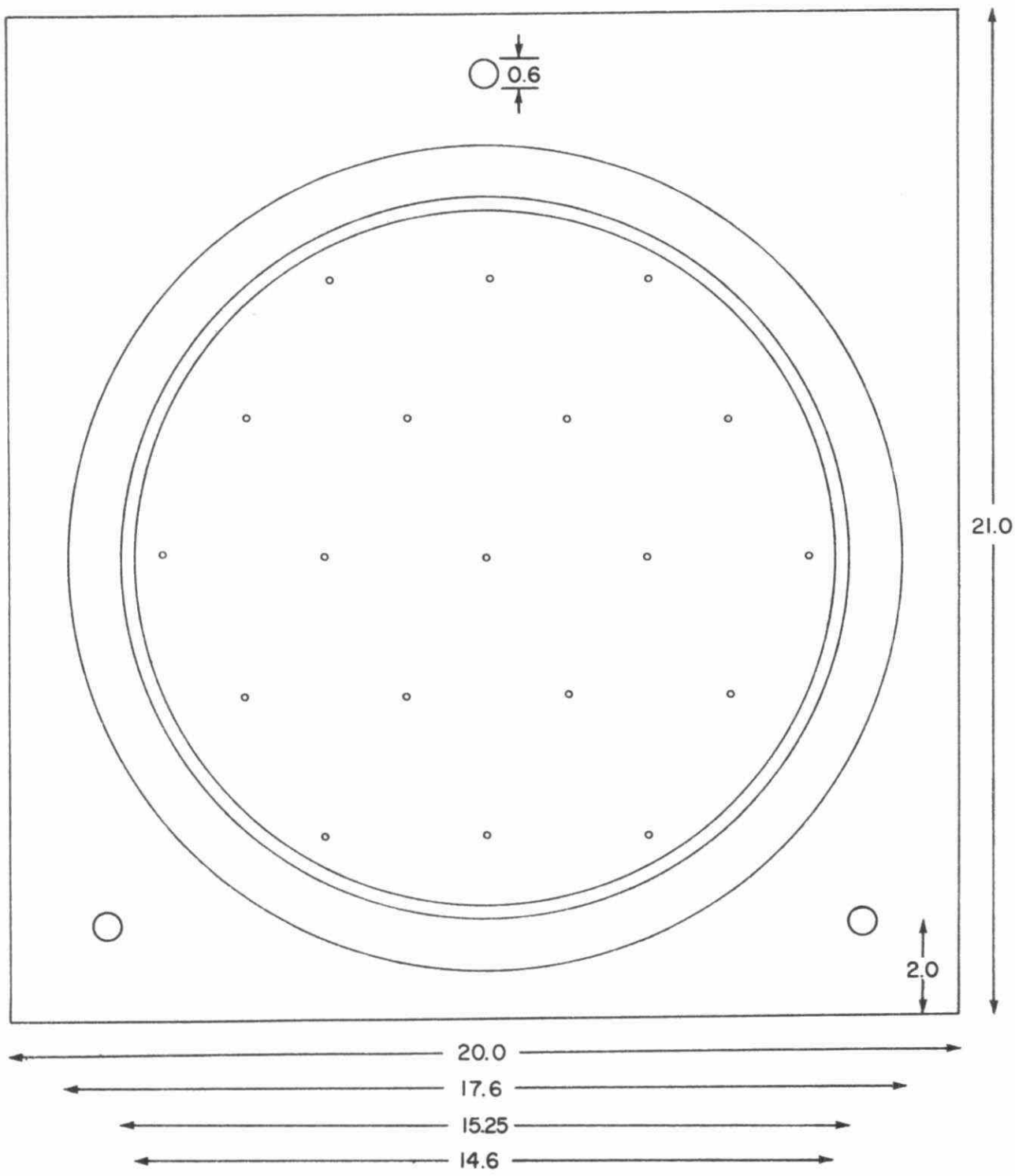
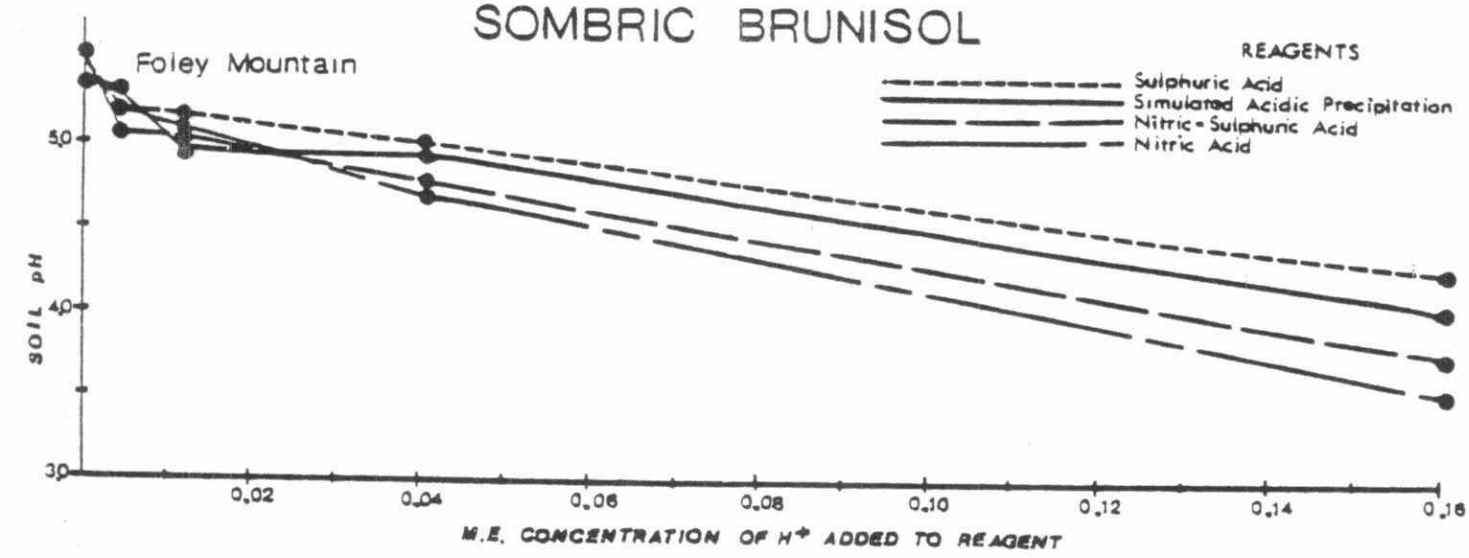


Figure 5. Application apparatus for soil leaching experiments.

(dimensions in centimetres)

Figure 6. Distribution of capillary tubes in bottom plate of lower reservoir.
(dimensions in centimetres)





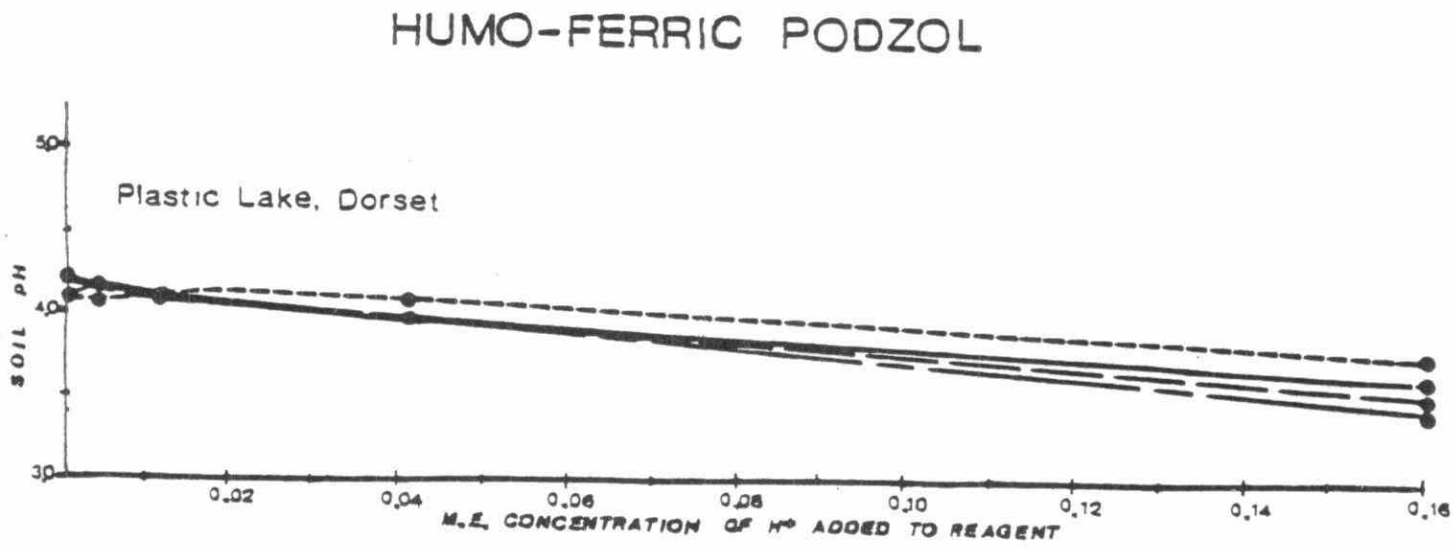


Figure 7. Examples of soil buffering curves of Ah horizons.

C. BIOGEOCHEMICAL STUDY

INTRODUCTION AND OBJECTIVE

One of the methods currently used to study the environmental effects of acid precipitation is the watershed approach, in which an ecosystem is selected for study based on an area defined by a stream or river drainage basin. The establishment of biogeochemical studies in watersheds so identified is a key component of the investigation of the terrestrial effects of acid rain in Ontario.

The objective of biogeochemical studies is to document element and nutrient distribution and cycling within forested ecosystems subjected to varying degrees of acidic deposition, and to determine the role of forested ecosystems in the process of lake acidification. To achieve the objective, representative components of the ecosystem being investigated must be quantified. From these measurements, simple models of terrestrial ecosystems can be developed, and gains, losses, and cycling of elements within and between the various components in the system can be estimated. By comparing data for areas subjected to different acid loadings, the effects of acidic inputs on the chemistry and biology of the forested ecosystem may be predicted. At each study site, incident precipitation, precipitation throughfall and precipitation stemflow is measured and analysed. Air quality and meteorology is also monitored, and litter collectors, soil lysimeters and piezometers are installed to enable ionic balances to be produced. Standing crop biomass and soil mass will be determined to assess nutrient storage and accumulation. Weirs or flumes are required to calculate a mass balance for each study area. Study sites are located near Dorset, Sudbury and Thunder Bay.

The purpose of this manual is to standardize the methodology used at the biogeochemical sites in Ontario. Since the forest types available for study are not uniform across the province,

some aspects of the recommended methodology are non-specific, especially with respect to numbers and deployment of monitoring devices. As far as possible, however, field equipment, investigative procedures and sample analysis are standardized throughout all study areas.

SITE SELECTION CRITERIA

The following criteria were considered in selection of biogeochemical study sites, bearing in mind that not every site met all criteria:

1. Each study area was to be readily defined within the drainage basin of a headwater stream which flows during a significant part of the non-winter season. The presence of ponds or swamp conditions along the course of the stream monitored could create problems in data interpretation. The recommended size for a study watershed was between 25 and 150 hectares.
2. The two northern Ontario sites were to be as similar as possible in vegetation composition, particularly with respect to tree species.
3. Soil in each area was to be "sensitive" to acidification (sandy, low cation exchange capacity).
4. Study sites were to be subjected to different acidic deposition loading.
5. Study sites should, if possible, have similar histories with respect to fire and harvesting. Historical environmental data would be useful.
6. All sites were to be accessible year round, preferably by road, and not influenced by local contaminant sources such as well-travelled unpaved roads. Sites were to be available on long-term tenure and free of potential vandalism. Access to electric power and a telephone line was desirable.

SITE DESCRIPTION

Detailed descriptions were prepared for all study sites. Site descriptions included a compilation of the following information:

1. Maps: topographical, geological, drainage systems, soil types, etc.
2. Photographs: aerial as well as ground level.
3. Vegetation cover: a plant species inventory list, tree stocking density, ground flora assessment and tree age distribution.
4. Soil type and depth description (Canadian Soil Classification System)
5. Geographic location (UTM coordinates).
6. Climate: annual rainfall, temperature, seasonal wind roses.

To aid in preparing maps delineating the waterhsed area and its feature, a reference grid of 100-metre intervals, coincident with established UTM lines, is useful. The reference grid can be used for establishing soil depths needed to determine total soil mass as well as other features. The following method of establishing a reference grid is recommended. A known reference point (A) is established in or near the watershed and is coincident with a UTM (100-m) coordinate intersection. A reference line (B) north and south of this point is established to the limits of the watershed and marked at 100-metre intervals. A second reference line (C) running east and west is similarly established. From these lines, the entire watershed is covered with reference points (D) at 100-metre intervals. Figure 8 (page 42) illustrates this procedure.

MONITORING METHODS

The parameters to be monitored at biogeochemical study sites have been selected to fit an ecosystem model comprising several

different elemental cycles. These parameters can be placed into the following four groups according to sampling frequency:

	Frequency	Measurement
1.	Once only	Watershed area, vegetation biomass, soil mass.
2.	Precipitation event	Incident precipitation, precipitation throughfall, precipitation stemflow, lysimeter leachate.
3.	Fixed interval	Incident precipitation, dry deposition, litterfall, stream water, evaporation rate, groundwater.
4.	Continuous	Stream flow-rate, SO_2, O_3, NO_x, meteorological measurements (wind speed, wind direction, etc.)

Some parameters may be measured with one instrument at a single site in the watershed (eg. air quality and meteorological data), while others require several samplers at different locations. Recommendations regarding sampling locations and equipment installation and operation are described in the following sections.

Watershed Area

The watershed area is determined to calculate elemental budgets. The area is established through perusal of topographic maps and aerial photographs, followed by ground observations. The watershed boundary is designated by permanent markers on the ground (eg. stakes and/or trees marked with flagging tape or paint) and shown on appropriate maps and aerial photographs. The final area is determined by planimeter or other suitable method.

Vegetation Biomass

Method to be determined.

Soil Mass

Method to be determined.

Incident Precipitation (Event)

Precipitation events are measured with a standard rain gauge and collected using an "Aerochem Metric" precipitation collector and precipitation throughfall collector. These samplers are installed according to siting criteria adopted for the APIOS deposition network. If a clearing of suitable area cannot be found in or near the watershed to be investigated, then the samplers are mounted on a tower above the tree canopy.

Samples are collected after each distinguishable rain period. This period may be less than an hour or may last for several days. Once the rain period has ended, samples are collected within 24 hours. Precipitation volume and pH are then measured and recorded and the sample submitted for analysis. Samples which cannot be submitted immediately to the laboratory are held under refrigeration until convenient for shipment.

Precipitation Throughfall

Throughfall is measured with polyethylene funnels, each approximately 650 cm^2 in collection area. The funnels have a vertical rim (finished to a knife-edge) to reduce splash effects, and are supported so that the rim is approximately 1 metre above ground level. The stem of the funnel is inserted into a plastic dustfall jar lid in which a hole of suitable size has been drilled. The inside of the jar is lined with a polyethylene bag to collect the sample. The funnel stem opening is covered with a nylon ("Nitex") screen of 100 mesh, and "Parafilm" is wrapped around the outside of the stem to seal the space between the stem and the hole in the dustfall jar lid.

Collectors are placed under representative tree species and tree size classes. To obtain samples representative of the given canopy, more than one collector may be required under large trees. In such cases, collectors are placed at different distances from the tree stem and pool the samples. Samples are collected as specified for event samples of incident precipitation. Samples are pooled for each tree monitored, volume and pH

is determined, and the samples are then submitted for analysis. Every 10 to 14 days, immediately after a precipitation event, funnels are removed for cleaning in the laboratory with "Acationox" (Canlab) detergent, followed by a triple rinse with distilled deionized water or equivalent. Funnels removed from the field for laboratory cleaning are replaced immediately with a spare set, to ensure collection of all dry deposition between events.

Throughfall under shrub canopies may be collected with a plastic trough placed on the ground. The trough may be fabricated from black, ABS 50 mm diameter piping or equivalent, split lengthwise. The trough may be a single length or have three or four side branches. A collection area of at least 0.25 m^2 is recommended. The trough is inclined slightly to conduct collected throughfall to a dustfall jar placed below ground level. The jar is lined with a collection bag of the same type specified for throughfall samplers. Figure 9 (page 43) illustrates one possible configuration.

Precipitation Stemflow

Stemflow is measured with collection collars attached to designated trees in the watershed. Sufficient collectors are used to adequately represent the different tree species and size classes occurring in the area.

A collection device consists of split "Tygon" tubing (Formulation R3603, ½ to 1-inch diameter) wound 1½ times around the tree stem between 1 and 2 metres above ground level, and drained into a collection vessel. To achieve good contact with a tree stem, some of the outer bark may be removed. The tubing is fastened to sample trees with stainless steel staples. After installation, a second cut is made in the tubing approximately 0.5 to 1 cm wide. The tubing is sealed to the tree stem with acrylic caulking. Stemflow from the tubing is collected in large plastic garbage cans lined with plastic garbage bags of suitable size.

The timing of sample collection is the same as that prescribed for incident event precipitation and precipitation throughfall. Collected samples, if large, may be weighed in the garbage can. A 475 ml-sample is removed for analysis and the remaining stemflow collected in the garbage can is poured on the ground around the bole of the tree sampled.

Lysimeter Leachate

Standardized ceramic disc-type tension lysimeters (15 cm diameter) are installed in the vicinity of representative tree species and size classes. Trees other than those sampled for throughfall and stemflow are selected for lysimeter studies and should be appropriately marked. A soil pit is dug under designated trees in the same manner specified for soil baseline studies. During this procedure, soil removed from different horizons is piled separately on plastic garbage bags or plastic sheets, to keep the surrounding area clean. Suitably cleaned lysimeter discs are installed in the middle of the A and B horizons and approximately 15 cm below the upper boundary of the C horizon. Cavities to insert the discs in the wall of the soil pit are made with minimum disturbance of the soil. Discs are installed horizontally, porous side up. A paste of soil and distilled water is applied to the upper surface of each disc to create a suction interface with the soil above. Discs in the different horizons are offset from one another so that no disc lies directly above another. After discs are installed, sample tubing is drawn to the surface, and soil is carefully returned to the pit in the reverse order from which it was removed. Tubing from each lysimeter disc is labelled, capped, and, if necessary, covered with protective material (eg. PVC piping) to prevent rodent damage.

Samples of lysimeter leachate are removed from the soil with a constant vacuum pump which applies a vacuum of approximately 0.1 bar across the lysimeter. Samples, whose volumes are individually recorded, are combined for a period of up to one week,

then preserved and submitted for analysis. Minimum sample size is 250 ml for TESX and 60 ml for SXITC test groups (see pages 33 and 34).

Incident Precipitation (Cumulative)

Where electric power is available, "Sangamo" precipitation samplers may be employed in the collection of cumulative samples at 28-day intervals, as specified for the APIOS deposition network. Sampling procedures adopted by the APIOS network are followed. Air Resources Branch staff is consulted for advice concerning sampling equipment to be installed at each watershed.

Low Volume Air Sampler

At study sites offering a power supply, monthly measurements of selected atmospheric nitrogen and sulphur compounds are made with a low-volume air sampler. The type of sampler and its operation is the same as that adopted for the APIOS network. The operation of a low-volume sampler may be omitted if a similar device is already present at a nearby APIOS deposition site.

Litterfall

Litterfall collectors consist of wooden frames supporting 1 mm mesh screening of a type to be developed. Each collection surface is either 0.5 or 1 m^2 in area and the wooden sides extend approximately 15 cm above the screening. The collector is positioned horizontally with the screen 15 cm above the ground.

Litterfall collectors are placed at each of the selected sample stations in each watershed. The collectors are located one-half of the distance between the trunk of the tree and the drip line of the tree. The selection of trees under which the collectors are placed should reflect the size distribution in the tree population.

Samples are collected monthly, except during the winter. The individual samples from each collector are to be separated

into leaves, twigs and other miscellaneous material, then dried and weighed. The leaves, twigs and miscellaneous material are treated as separate samples and are pooled from the various litterfall collectors for chemical analysis.

Stream Water

Measurement of stream flow rates and water chemistry are undertaken. Flow rates are monitored continuously at a stream gauging station which comprises a weir or flume, stilling well, and water level recorder. More than one weir may be considered for each biogeochemical site. If only one weir is used, it is located near the point where the stream leaves the study watershed. Water Resources Branch staff or specialist Regional staff is consulted for advice regarding weir installation and operation. Several technical publications are also available for guidance.

Samples for chemical analysis are collected once a week at a point approximately 10 metres upstream of the weir. During periods of high flows, more frequent sampling may be required to more accurately determine losses of ions and nutrients from the study area. Sampling and analytical procedures follow, as closely as possible, those used by Water Resources Branch at the Dorset study sites.

Evaporation Rate

An estimate of water lost from the study area by evaporation and transpiration is required to establish a water budget. Evapotranspiration can be estimated from temperature data with the Thornthwaite system. Evaporation may be determined with standard Class A evaporating pans. Water Resources Branch staff should be consulted for advice.

Groundwater

Studies are undertaken to monitor water table levels and groundwater quality. Because soil features (especially depth to bedrock) may vary significantly between sites, Water Resources

Branch or Regional staff are consulted before proceeding with equipment installation and measurements. If and when installed, piezometers assist in determining a water budget for the watershed. Groundwater level measurements and groundwater samples for chemical analysis are obtained at least once a month.

Air Quality Monitoring

Continuous measurements of SO_2, O_3, and NO_x in ambient air are obtained with monitors approved by the Ministry and housed in a suitable shelter at a site in or near the study area. The contractor operates the monitors under the direction of Ministry staff, but repairs and audit calibrations are carried out directly by the Ministry. If existing monitors are already in operation in the vicinity, monitors may not be required at the biogeochemical site.

Meteorological Measurements

In addition to precipitation measurement and analysis, continuous monitoring of wind speed and wind direction is recommended. Every effort is made to comply with accepted criteria for siting wind monitoring equipment. Significant interference from the forest tree canopy and local geographical features is minimized.

Other meteorological data which may benefit the biogeochemical study include air temperature and relative humidity, net radiation, soil temperature, and measurements of precipitation periods and precipitation intensity.

WINTER PROGRAM

Most of the field work at the biogeochemical study areas is suspended during winter months. However, some studies continue during this period, and the sites are visited fairly frequently (perhaps weekly) to undertake the following work:

(a) Performance of routine checks on all continuous air quality and meteorological monitoring equipment (including electric generators, if used).

(b) Performance of routine checks on stream flow recording equipment.

(c) Regular measurements of snow pack depth throughout the watershed area. Snow core samples are collected, following normal Ministry sampling procedure, just prior to and during the spring snow melt period.

(d) Measurement of snowfall at weekly intervals. Open-top stemflow collection vessels may be suitable for this purpose.

Data Records

To ensure completeness of records of the biogeochemical study, the following suggestions are offered as a guide:

(a) Photographs of equipment installations throughout the study area.

(b) Maintenance of a visit log book to record details of study activities, including unusual observations. Separate log books will also be maintained for use with all continuous monitoring equipment.

(c) Appropriate sample shipment records, chemical analysis request forms (LIS), and records of precipitation sampling.

(d) All data forms for the biogeochemical study are standardized throughout the province.

Submission of Samples for Chemical Analysis

All sample locations are identified with a 7-digit code compatible with the location codes assigned under the Ministry's laboratory information system (LIS).

Samples are collected and submitted in accordance with procedures outlined in the Ministry's "Outline of Analytical Methods" (1981, Laboratory Services and Research Branch), in the "Field Procedures Manual" (1983, Air Resources Branch) and in the APIOS "Terrestrial Effects Procedures Manual" (1983), unless specifically instructed otherwise. Each sample is identified with its own number, from a series allocated by Phytotoxicology Section, Air Resources Branch, and is submitted on LIS "Request for Analysis" forms.

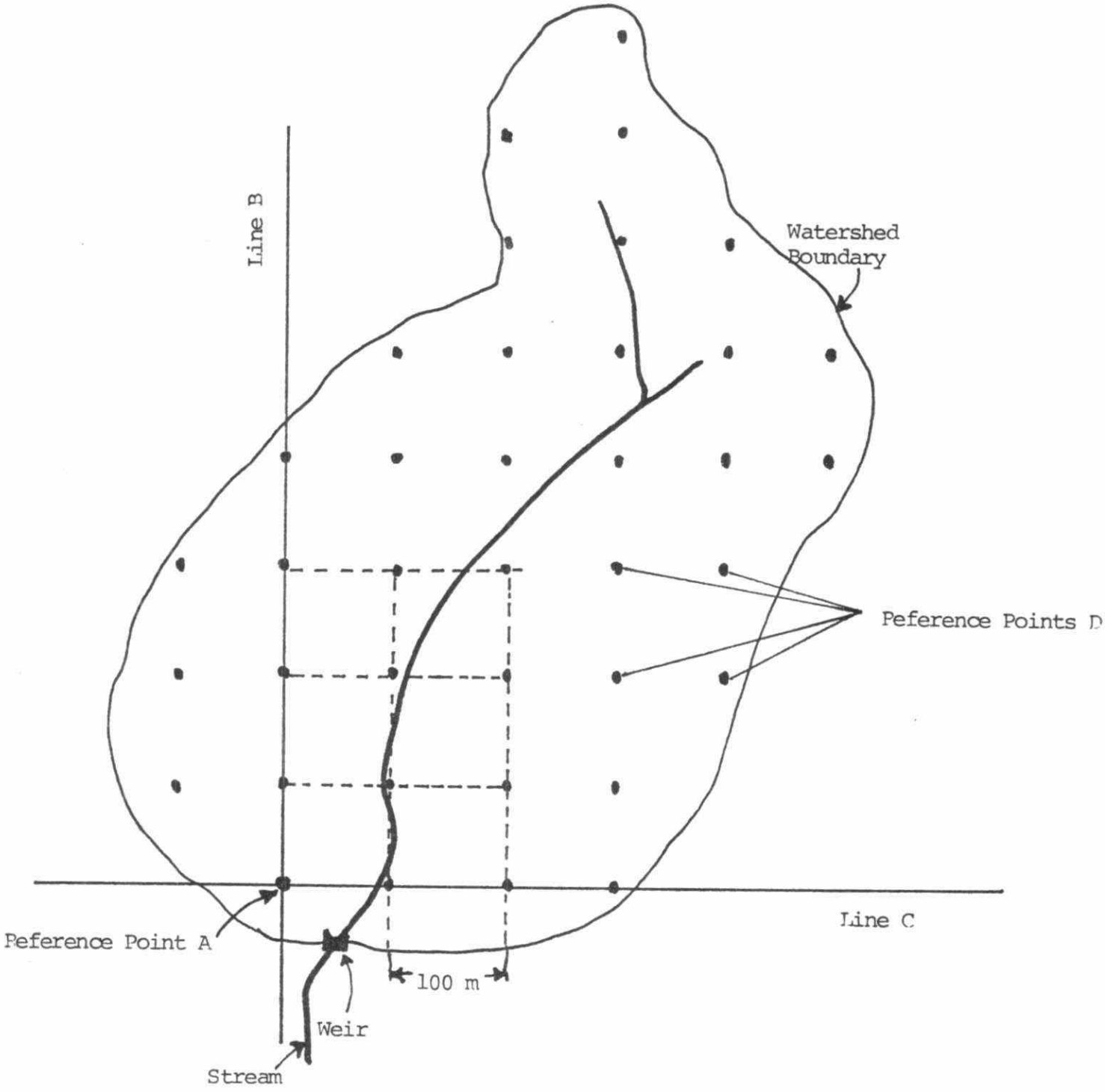
All aqueous samples to be analyzed for trace metals are filtered through a 0.45 micron "Millipore" filter, preserved with sufficient ultra pure concentrated HNO_3 to obtain a solution of 1% HNO_3 in the sample (approximately 20 drops per 60 ml sample, or 10 drops per 30 ml sample), and submitted in 100-ml plastic vials prepared in advance by the Ministry's Toronto Laboratory. All aqueous samples are refrigerated until shipped. Batches of incident and throughfall precipitation samples may be submitted under one submission number, but stemflow, leachate and stream-water sample batches are each submitted separately. The following tests are performed on all aqueous samples except soil leachate: total soluble Al, Fe, Mn and Zn, volume, pH, Gran acidity, unfiltered reactive SO_4, Cl, NO_3, Ca, Mg, Na, K, NH_3 and PO_4. The corresponding LIS test groups are SXITC for soluble trace metals and TEWQ for the remaining parameters. The test names for SXITC are: ALUT, MNUT, FEUT, ZNUT. For TEWQ, the names are: VOLUME, PH, ACDG, SSO4UR, CLIDUR, NNO3UR, CAUR, MGUR, NAUR, KKUR, NNHTFR and PPO4FR.

Aqueous samples of leachate from lysimeters and from soil column leaching experiments are analysed for test groups SXITC and TESX. TESX includes: pH, Ca, Mg, Na, K, SO_4, NO_3, and Cl. The TESX test names are: pH, CAUR, MGUR, NAUR, KKUR, SSO4UR, NNOTFR, and CLIDUR.

All soil samples are initially analysed for pH-water, pH-$CaCl_2$, exchangeable calcium, magnesium, potassium and aluminum; cation exchange capacity; dithionite extractable iron, aluminum

and manganese; sodium pyrophosphate extractable iron, aluminum and manganese; organic carbon, soluble aluminum, water soluble sulphate, total nitrogen, total carbonates, acid extractable copper, nickel, lead and zinc, particle-size and plant available phosphorus. The LIS test groups for these analyses are TEAPS I and TEAPS 6, and the LIS test names (in the same order as above) are: PHEW, PHECA, CAESC, MGESC, KKESC, ALESC, CEC, FEEDI, ALEDI, MNEDI, FEEPY, ALEPY, MNEPY, COD, ALECA, SSO4EW, NNTKUR, CCO3UR, CUUT, NIUT, PBUT, ZNUT, SAND, SILT, CLAY and PPO4SB. Later in the study, as information on soils from biogeochemical sites is accumulated, the number of analytical tests may be reduced.

Vegetation, including litterfall, is analysed for total P, K, N, Cl, S, Ca, Mg, Na, Al, Mn, Fe, Cu, Zn, Mo, Ni, Pb, Cd. The LIS test group is TEAPS 5 and the test names are: PPUT, KKUT, NNTKUR, CLUT, SSUT, CAUT, MGUT, NAUT, ALUT, MNUT, FEUT, CUUT, ZNUT, MOUT, NIUT, PBUT, and CDUT.



Method for establishing a reference grid on a hypothetical watershed

Figure 8

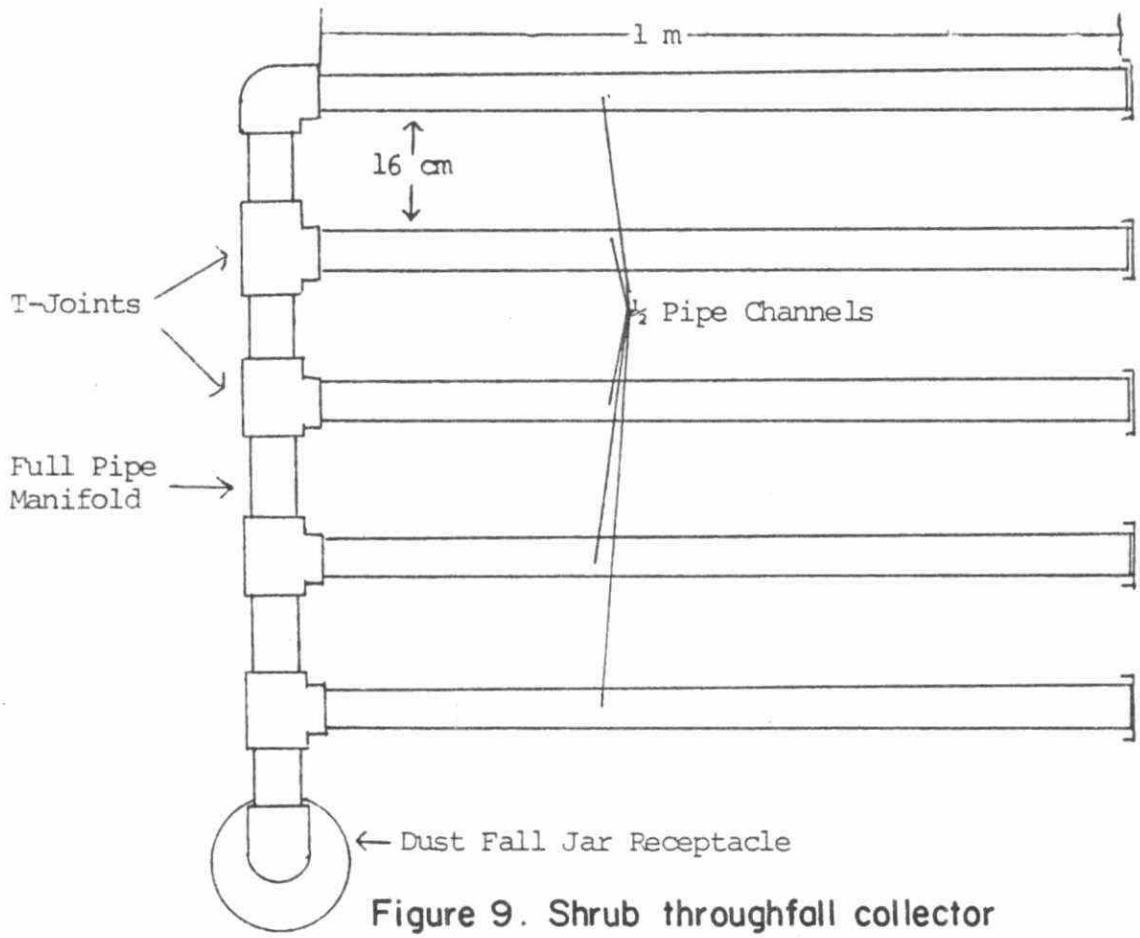
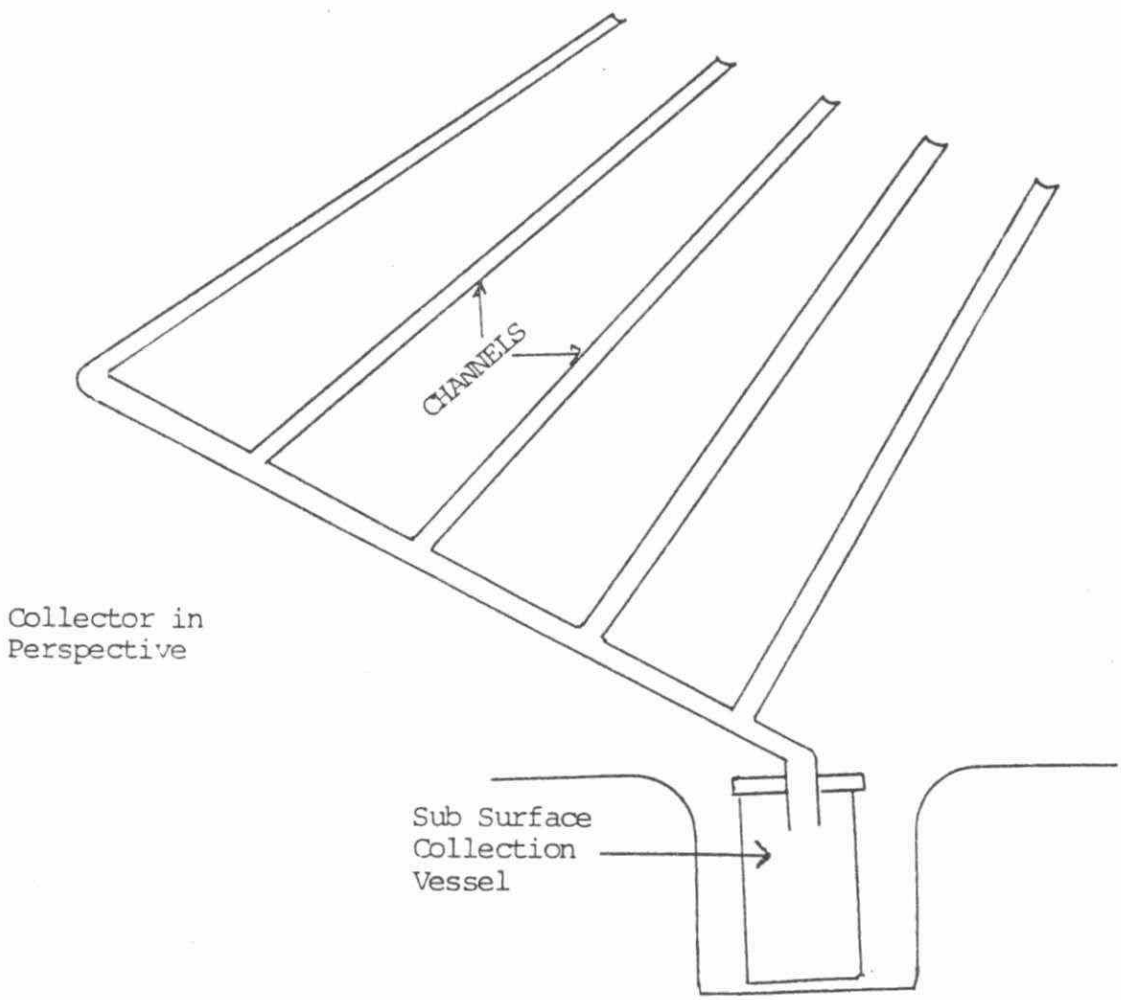


Figure 9. Shrub throughfall collector



D. LABORATORY ANALYSIS

INTRODUCTION

The sample workload for the Terrestrial Effects Studies, Acid Precipitation in Ontario Study (APIOS), is split between the Water Quality Section (WQS) and the Inorganic Trace Contaminants Section (ITC) at the Ministry's Laboratory Services Branch, Resources Road, Rexdale.

The ITC Section analyses all APIOS soil and vegetation samples as well as aqueous samples requiring trace metals analysis. A brief outline of these methods is given in the following pages. For more detailed descriptions of the methods of soil analysis, contact Anne Neary, ITC Section, Laboratory Services Branch, Resources Road, Rexdale.

WATER SAMPLES

Total Iron, Zinc, Manganese and Aluminum

(LIS test names: FEUT, ZNUT, MNUT, ALUT)

Incident precipitation (preserved with 5% HNO_3), field filtered throughfall, stemflow and lysimeter leachates (preserved with 1% NHO_3) are first analysed for Fe, Zn, Mn and Al by inductively coupled plasma atomic emission spectroscopy (ICP). Elements found to be below the ICP detection limit are then analysed by graphite furnace flameless atomic absorption. A more exhaustive metals scan is usually performed on incident precipitation samples. A detailed description of metals analysis is found in the Ministry's "Handbook of Analytical Methods for the Analysis of Environmental Samples", which is currently in press. Copies of a specific method may be obtained from the Water Quality Section, Resources Road laboratory.

Other Parameters

Aqueous samples are analysed by WQS for all paramaters except trace metals (most commonly Fe, Al, Mn and Zn). In addition, WQS also determines the percent total organic carbon in soil samples. A detailed description of all methods employed by WQS may be found in the handbook referred to in the preceding section.

SOIL SAMPLES

pH

(LIS test names: PHEW, PHECA)

pH is defined as the negative logarithm of the hydrogen ion concentration and is a measurement of hydrogen ion activity. The expression of pH in logarithmic units means that a change in pH of one unit represents a tenfold change in H^+ concentration. The pH is one of the most informative soil characteristics and may indicate possible nutrient toxicity or deficiency.

A 10 g sample of air-dried soil, ground to less than 2 mm, is weighed into a beaker and 20 ml of distilled water are added (PHEW). Samples are stirred intermittently for 30 minutes and left to equilibrate for 30 minutes. The pH is then determined electrometrically. The test is repeated using 0.01 M $CaCl_2$ instead of distilled water (PHECA). The $CaCl_2$ reduces interference due to liquid junction potential, flocculates the soil to reduce interference from suspended material, standardizes the electrolyte concentration and brings it closer to that of the soil solution, decreases the electric double layer so that the solution pH more closely represents soil pH, and has a pH closer to rainwater in equilibration with atmospheric CO_2. Because of the advantages of the $CaCl_2$ method, pH measured in distilled water is primarily used for comparison with historical data.

References:

McKeague, J. A. 1978. Manual on soil sampling and methods of analysis. 2nd ed. Canada Soil Survey Committee on Methods of Analysis, Ottawa; 66-68.

Hesse, P. R. 1971. Soil chemical analysis. John Murray Pub. Ltd. London; 19-36.

Particle Size

(LIS test names: SAND, SILT, CLAY)

Particle size is one of the most stable soil characteristics and controls porosity, permeability, water holding capacity, leaching potential, exchangeable cations, cation exchange capacity, weathering behaviour, and geotechnical aspects of the soil. It is a useful parameter when determining the sensitivity of soil to acid rain.

The measurement of particle size is restricted to the inorganic phase and is carried out by pipette analysis. A 10 g sample of air-dried soil, ground to less than 2 mm, is pretreated for carbonate and organic matter removal using sodium acetate (pH 5) and hydrogen peroxide, respectively. The remaining sample is dispersed with Na-hexametaphosphate-Na-carbonate and the sand fraction (<53 μm) is removed by wet sieving and is then dried and weighed. Measurement of the silt and clay fraction is based on Stoke's Law of settling velocity. Particles of a specific average size are collected by pipetting aliquots from predetermined depths at predetermined times. Samples are dried and weighed. Percentage sand (>53 μm), silt (53-2 μm) and clay (<2 μm) are calculated.

References:

Day, P. R. 1965. Particle fractionation and particle size analysis. Methods of soil analysis. Part 1. C. A. Black et. al. (eds.) Agronomy Monograph No. 9, Madison, Wisconsin: 545-567.

Green, A. J. 1978. Particle size analysis. Manual on soil sampling and methods of analysis. J. A. McKeague (ed.). Canada Soil Survey Committee on Methods of Analysis, Ottawa; 4-13.

Total Carbonates

(LIS test name: CCO3UR)

Carbonates occur naturally in soils, usually in the form of calcite and dolomite (calcium and magnesium carbonates), although many other forms may exist. Carbonates are not usually present in significant amounts in soils whose pH less is than 7 and are non-existent in soils whose pH is less than 5. Because carbonate neutralizes acid, its measurement is important in acid rain studies.

A 0.500 g air-dried sample, ground to less than 150 µm (100 mesh), is weighed into a flask. Carbonates are determined from the volume of CO_2 produced by the reaction of the carbonate in the sample with 6N HCl in a closed system under constant temperature and pressure. The system is first calibrated with calcium carbonate, and MnO_2 interference is overcome by the addition of FeCl, which ensures the reduction of MnO_2 without the production of Cl_2.

References:

Allison, L. E. and C. D. Moodie. 1965. Carbonates methods of soil analysis. Part 2. C. A. Black et. al. (eds.). Agronomy Monograph No. 9, American Society of Agronomy, Madison, Wisconsin; 1388-1392.

Driemanis, A. 1962. Quantitative gasometric determination of calcite and dolomite using Chittick apparatus. J. Sedimentary Petrology 32(3): 520-529.

Exchangeable Cations and CEC

(LIS test names: CAESC, KKESC, MGESC, ALESC and CEC)

The capacity of clays and organic matter for the surface adsorption of large amounts of cations is due to the charge deficiency created by isomorphous substitution within the clay lattice sheets, the dissociation of hydroxyl groups from the edges of clay minerals, and the dissociation of functional groups from weak acids present in organic matter. The levels of exchangeable cations and the cation exchange capacity affects the buffering capacity of the soil, the level of plant-available nutrients, and may be important when determining the potential of the soil for acidification.

Exchangeable cations and permanent charge CEC are measured at the pH level of the soil, using 2N NaCl. A sample of air-dried soil, ground to less than 2 mm, is shaken with 2N NaCl for 4 h to allow Na ions to replace ions in the exchange complex. The sample is centrifuged, filtered, and the extract analysed by atomic absorption spectrophotometry for Ca, Mg, K (and Al if the soil pH is below 5.5). Results are converted to me/100 g and the CEC is reported as the sum of the cations measured.

Aluminum is used as the measure of the acidic component. The pH dependent plus permanent charge CEC has also been measured using a buffered solution and a separate test for exchangeable H^+. However, the 2N NaCl method is better suited to large numbers of samples, provides probably the most unambiguous information on soil exchange characteristics under field conditions, and is better related to plant-available cations. A disadvantage is that Na^+ cannot be determined. However, for most Ontario soils, Na^+ contributes little to the CEC.

References:

Grove, J. H., Fowler, C. S. and M. E. Sumner. 1982. Determination of the charge character of selected acid soils. J. Soil Sci. Soc. Amer. 46: 32-38.

Osborne, V. E. 1978. Cation exchange capacity and exchangeable cations. Manual on soil sampling and methods of analysis. J. H. McKeague (ed.). Canada Soil Survey Committee on Methods of Analysis, Ottawa; 72-75.

Organically-Bound Iron, Aluminum and Manganese

(LIS test names: FEEPY, ALEPY, MNEPY)

Sodium phyrophosphate has been found to extract humus and its complex Fe and Al salts and has little effect on amorphous or crystalline inorganic Fe and Al oxides. Pyrophosphate-extractable Fe and Al have been incorporated by the National Soil Survey Committee of Canada into their classification scheme. A 0.3 g sample of air-dried soil, ground to less than 150 µm is shaken overnight with 30 ml of 0.01 M Na-pyrophosphate. Samples are centrifuged at 20,000 rpm and the supernatant decanted and analysed for Fe, Al and Mn by atomic absorption spectrophotometry. Results are reported as percent dry weight.

References:

Bascomb, C. L. 1968. Distribution of pyrophosphate extractable iron and organic carbon in soils of various soil groups. J. Soil Sci. 19: 251-268.

McKeague, J. A. 1978. Manual on soil sampling and methods of analysis. 2nd ed. Canada Soil Survey Committee on Methods of Analysis, Ottawa; 104-105.

Oxides and Organically-Bound Forms of Iron, Aluminum and Manganese

(LIS test names: FEEDI, ALEDI, MNEDI)

Finely divided hematite and goethite, amorphous oxides of Fe, Al and Mn, and organically complexed forms of these metals can be extracted with a citrate-bicarbonate-dithionite solution. This method has been incorporated by the National Soil Survey

Committee of Canada into their classification scheme for characterizing podzolic soils in Canada. An aliquot of air-dried soil, ground to less than 100 mesh, is extracted at 80°C with a sodium citrate-sodium bicarbonate-sodium dithionite solution. Sodium chloride is added to flocculate the sample. Samples are centrifuged at low speed and the supernatant decanted. Samples are extracted again, then washed twice. The final volume of extractant is diluted and Fe, Al and Mn are determined by atomic absorption spectrophotometry. Results are reported as percent dry weight.

References:

Mehra, O. P. and M. L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals 5: 317-317.

McKeague, J. A. and J. H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46: 13-22.

Trace Metals

(LIS test names: CUUT, ZNUT, NIUT, PBUT)

Zinc, copper, nickel and lead occur in soils in amounts which vary with changing organic matter and clay content, pH, and parent material or bedrock type. These metals are determined by atomic absorption spectrophotometry after sample extraction with nitric and perchloric acids. This extraction does not remove those metals bound in silicate matrices and certain refractory oxides. The analysis, therefore, does not determine total metals, but the fraction recovered is thought to be more environmentally significant with respect to acid rain inputs to a soil system. A 0.5 g sample of air-dried soil, ground to less than 100 mesh, is heated with HNO_3-$HClO_4$ in a hot-block digester for 2 h at 120°C and then at 175°C for about 5 h, until 1 ml of liquid remains. Samples are diluted to 25 ml, centrifuged, and analysed for Cu, Zn, Ni and Pb.

References:

Bock, R. 1979. Decomposition methods in analytical chemistry. International Textbook Co. Ltd. London; 212-232.

Hesse, P. R. 1971. Soil chemical analysis. John Murray Pub. London; 371-374.

Available Phosphorus

(LIS test name: PP04SB)

Phosphorus occurs in soils in both organic and inorganic forms. It is in the inorganic form (primarily orthophosphate) that phosphorus is readily available to plants. Organic phosphorus is not utilized by plants directly but it is mineralized by enzyme activity to become a potential source of available phosphorus. To measure available phosphorus, 1 g of air-dried soil, ground to less than 2 mm, is shaken for 30 minutes with 0.5 M $NaHCO_3$. A teaspoon of carbon black is added prior to shaking to remove colour (a blank is run with the extractant and the carbon). Samples are filtered and P is measured colorimetrically on the extracts after dilution.

References:

Olsen, S. R., Cole, C. V., Watanabe, F. and L. A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular No. 939, Washington, D. C.

Hesse, P. R. 1971. Soil chemical analysis. John Murray Pub. London; 255-300.

Available Aluminum

(LIS test name: ALECA)

The analytical method presently used by the Ministry removes a fraction of aluminum which strongly correlates with aluminum uptake by plants and its adverse effects on crop yields. These

data may be valuable to studies on the effects of acid rain on soil. A sample of air-dried soil, ground to less than 2 mm, is shaken for 5 minutes with 0.01 M $CaCl_2$ (2:1, solution:soil ratio). The samples are centrifuged, filtered, and the extracts are acidified and analysed for aluminum by atomic absorption spectrophotometry. Manganese may also be determined in the extract: studies have found that this fraction of manganese correlate well with manganese uptake by plants.

References:

Hoyt, P. B. and M. Nyborg. 1971. Toxic metals in acid soil: I. Estimation of plant-available aluminum. Soil Sci. Soc. Amer. Proc. 35: 236-240.

Hoyt, P. B. and M. D. Webber. 1974. Rapid measurement of plant-available aluminum and manganese in acid Canadian soils. Can. J. Soil Science 54: 53-61.

Mineralogical Analysis

(LIS test name: XRD)

The mineralogical composition of a soil largely controls its chemical properties and behaviour. The weathering products, susceptibility to weathering, mechanical behaviour, buffering capacity, cation exchange capacity and available nutrient supply of the soil are some of the parameters which are a function of a soil's mineralogy.

A powder pattern of the whole sample is first prepared and X-rayed to determine the dominant minerals present in the sand and silt fraction. To determine the mineralogy of the clay fraction, the clay is separated as described in the particle size method, after pretreatment for organic matter and carbonate removal. Two aliquots of the clay fraction are removed. One aliquot is saturated with Mg^{2+} and one with K^{+} to facilitate distinction between chlorite and vermiculite. The aliquots are passed through a membrane filter so that the clay remaining on

the filter is oriented to permit better resolution of the clay peaks. Since most clay minerals are poorly crystalline, orienting the clay platelets improves the diffraction pattern. The clay is then transferred from the membrane filter to a glass slide by inverting the filter on the slide and applying pressure. The slides are air-dried and X-rayed. Depending on the peaks obtained, the slides are glycol-saturated and/or heat treated and X-rayed again. The mineralogy of the sample is determined through interpretation of the powder pattern and four X-ray traces of the clay fraction.

References:

Brown, G. 1961. The X-ray identification and crystal structure of clay minerals. Mineralogical Society of London.

Carroll, D. 1970. Clay minerals: A guide to their X-ray diffraction. Geological Society of America. Special Paper 126. Colorado, U. S. A., p. 80.

Whittig, L. D. 1965. X-ray diffraction techniques for mineralogical identification and mineralogical composition. Methods of soil analysis. Part 1. C. A. Black et. al. (eds.). Agronomy Monograph No. 9, American Society of Agronomy, Madison, Wisconsin; 671-698.

Soil-Acid Equilibration (Buffering Curve)

(LIS test name: BUFCRV)

This method was devised specifically for the APIOS Terrestrial Effects program to examine the ability of a soil to buffer inputs of sulphuric acid. Nine, 10 g aliquots of air-dried sample, ground to less than 2 mm, are weighed into separate beakers. Twenty ml of distilled water is added to the first beaker and 20 ml of varying concentrations of sulphuric acid are added to the remaining beakers (me concentrations vary from 0.02 me for 20 ml of 0.001 N H_2SO_4, to 1 me for 20 ml of 0.05N H_2SO_4). Samples are stirred for 30 minutes, left to equilibrate for 1 h,

and pH is then determined. Results are plotted (pH vs me concentration) with each aliquot representing a point on the curve. This method avoids dilution problems associated with a regular titration. The equilibrating solution can be altered, if desired, to more accurately reflect the ion concentrations of acid precipitation in Ontario.

Soluble Sulphate

(LIS test name: SSO4EW)

Sulphate is an important ion in the Terrestrial Effects Study because it is added to the soil by the precipitation itself as well as through mineralization of organic sulphur compounds. Water-soluble, plant-available sulphate is extracted by shaking a 5 g sample of air-dried soil, ground to less than 2 mm, with 25 mℓ of distilled water. Although saturated pastes and 2:1 solution:soil ratios have also been used, the 5:1 ratio was chosen as it accomodates highly organic samples and yields enough sample to permit membrane filtration. After being shaken for 1 h, samples are centrifuged and filtered through a 0.45 μ membrane filter. Extracts are analysed for SO_4 by ion chromatography.

Reference:

Ballantyne, A. K. 1978. Soluble salts. Manual on soil sampling and methods of analysis. J. A. McKeague (ed.) Canada Soil Survey Committee on Methods of Analysis, Ottawa; 71.

Total Nitrogen

(LIS test name: NNTKUR)

Nitrogen compounds are converted to simple inorganic forms (ammonium ions) by sample dissolution in sulphuric acid and potassium persulphate. A sample size of 0.08 g to 0.4 g is required, air-dried and ground to less than 2 mm. The potassium presulphate increases the boiling point and provides an oxidizing

environment. Iron and calcium interference is removed by filtration, after making the solution strongly basic. Ammonia is analysed colorimetrically in the digestate.

Reference:

Ontario Ministry of the Environment. 1981. Outlines of analytical methods. Water Quality Section Laboratory Services Branch. pp. 246.

Total Organic Carbon

(LIS test name: COD, OXMAT)

Carbon is the major element in soil organic matter. Organic carbon (COD) in APIOS soils is determined on a 0.01 g to 0.10 g aliquot of air-dried soil, ground to less than 150 µm (100 mesh). Sample size depends on the organic carbon content of the soil, estimated by soil colour. The organic carbon in the sample is oxidized by the addition of a sulphuric acid - potassium dichromate - mercuric sulphate - silver sulphate mixture and samples are digested in an oven at 150°C for 3 hours. The digestate is cooled, then analysed for colorimetrically for CR III. Results are converted to percent total organic carbon.

Samples for which comparisons with historical data were to be made, were also analysed for organic carbon by the Walkley-Black method (OXMAT). Samples are digested with sulphuric acid and potassium dichromate using only the heat of the reaction. Excess dichromate is determined by titration with ferrous ammonium sulphate. The percent oxidizable organic carbon is calculated and results are converted to total organic carbon by multiplying by a factor of 1.33 (determined through studies on U. S. soils).

Reference:

Allison, L. E. 1965. Organic carbon. Methods of soil analysis. Part 2. C. A. Black et al. (eds.) Agronomy Monograph No. 9, American Society of Agronomy, Madison, Wisconsin; 1367-1378.

Crowther, J. and K. Clarke. 1982. Semi-automated determination of chemical oxygen demand. Internal Report. Ontario Ministry of the Environment Laboratory Services Branch, Rexdale, Ontario.

VEGETATION SAMPLES

Total Calcium, Potassium, Chlorine, Phosphorus and Sulphur

(LIS test names: CAUT, KKUT, CLUT, PPUT, SSUT)

These nutrients are all measured in a vegetation pellet by X-ray fluorescence spectrometry. A sample of dried, ground vegetation is weighed into a clean plastic vial. Powdered wax is added to the vial, the vial is capped, then shaken until a homogenous mixture is obtained. The mixture is transferred to a die and pelletized with a pressure of 25 tons. Samples are analysed for total S, Ca, K, Cl and P by X-ray fluorescence spectrometry.

References:

Judge, R. H. and J. A. Pimenta. 1980. The analysis of plant material by X-ray fluorescene spectrometry, Part 1: chlorine, sulphur, phosphorus, calcium, potassium, silicon. Ministry of the Environment, Laboratory Services Branch, Rexdale, Ontario.

Norrish, K. and J. T. Hutton. 1977. Plant analysis by X-ray spectrometry: low atomic number elements, sodium to calcium. X-ray spectrometry. 6(1): 6.

Total Magnesium, Sodium, Aluminum, Manganese, Iron, Copper, Zinc, Molybdenum, Nickel, Lead and Cadmium

(LIS test names: MGUT, NAUT, ALUT, MNUT, FEUT, CUUT, ZNUT, MOUT, NIUT, PBUT, CDUT)

A sample of dried, ground vegetation is weighed into a crucible and ashed in a muffle furnace at a temperature below 150°C. The temperature is then raised to 250°C for 1 h, and to

500°C for 3 h. The sample is then digested in aqua regia at moderate heat. The digestate is diluted with distilled water and analysed for Mg, Na, Al, Mn, Fe, Cu, Zn, Mo, Ni, Pb and Cd by ICP.

Reference:

Ontario Ministry of the Environment. Handbook of analytical methods for the analysis of environmental samples (in press). Laboratory Services Branch.

Total Nitrogen

(LIS test name: NNTKUR)

Nitrogen compounds are converted to simple inorganic forms (ammonium ions) by sample dissolution in sulphuric acid and potassium persulphate. A sample of approximately 0.02 g, dried and ground to <40 mesh, is required. The potassium persulphate increases the boiling point and provides an oxidizing environment. Iron and calcium interference is removed by filtration after making the solution strongly basic. Ammonia is analysed colorimetrically in the digestate.

Reference:

Ontario Ministry of the Environment. 1981. Outlines of analytical methods. Water Quality Section, Laboratory Services Branch. pp. 246.

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